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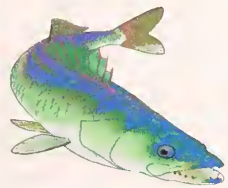
Ontario

MINISTRY OF ENVIRONMENT AND ENERGY
SCIENCE AND TECHNOLOGY BRANCH
AQUATIC SCIENCE SECTION



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# MERCURY IN ONTARIO'S ENVIRONMENT

## MERCURY IN ONTARIO SPORTFISH

Contaminants in Ontario's sportfish have been the subject of surveillance and monitoring for over 20 years. The program, carried out by the Environmental Monitoring and Reporting Branch (EMRB) of the Ministry of Environment and Energy with the assistance of the Ministry of Natural Resources, seeks to detect potentially dangerous accumulations of toxic substances in fish, and to report those occurrences to the public in the *Guide to Eating Ontario Sportfish*. While a number of organic substances are commonly found in fish from the Great Lakes, most contaminants are rare in inland lakes. The exception is mercury. Mercury has been found in fish virtually everywhere in Ontario, and has resulted in more consumption restriction than any other contaminant in the program. Mercury is the largest impediment on the usage of fish from inland lakes. Clearly, we need to understand it sources, factors that control its accumulation in fish, and its effects on the environment.

Concisely summarizing the status of mercury contamination in Ontario fish is complicated by several factors. The mercury concentration varies with size of fish, species and lake. Moreover, within a given size, there is significant variability or scatter among individuals. Because of this relationship a detailed examination of the impacts of mercury must take into account the effect of size on mercury concentration. Of particular concern is the frequency of occurrence of consumption restriction within certain size intervals of fish. Not all sizes of fish are used equivalently, and wildlife use different sizes than humans. Hence, potential impacts must take into account the concentration of mercury within specific size ranges on a species by species basis.

Using EMRB's sport fish contaminant database the frequency of contaminated populations of several species was determined for four size classes of fish. The results for two species are illustrated (Fig. 1), but results for other species

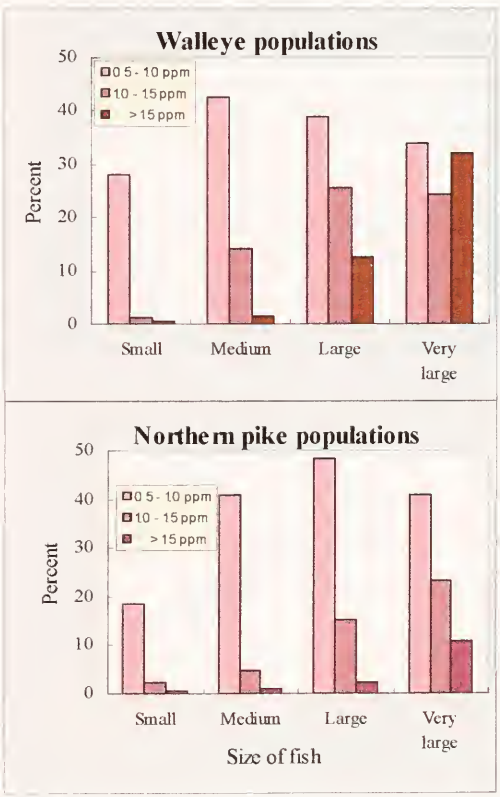


**Figure 1** Proportion of fish populations affected by mercury. The fish populations affected by mercury are not confined or grouped in any way within a particular portion of the province.

such as smallmouth bass and lake trout are similar. Size specific concentrations were used to classify the size category of the population within one of the following concentration ranges: <0.5 ppm, 0.5 - 1.0 ppm, 1.0 - 1.5 ppm, and >1.5 ppm mercury. These intervals correspond to the categories used in the *Guide to Eating Ontario Sportfish*. Frequency histograms of populations which fall into the three categories of restricted consumption are shown for several species in Fig. 1. Even in small fish the concentration of mercury exceeds the 0.5 ppm consumption guideline with appreciable frequency, and as the size increases exceedance becomes the rule rather than the exception. For example, based on large walleye, about 80 % of the populations are above 0.5 ppm and a significant portion (~10%) are above 1.5 ppm, the concentration at which no consumption is recommended. Clearly, mercury contamination of Ontario's sportfish is a common phenomenon.

Figure 2 shows the location of walleye lakes and those affected by mercury. Affected lakes are widely scattered across the province with their frequency of occurrence parallel to the frequency of sampling.

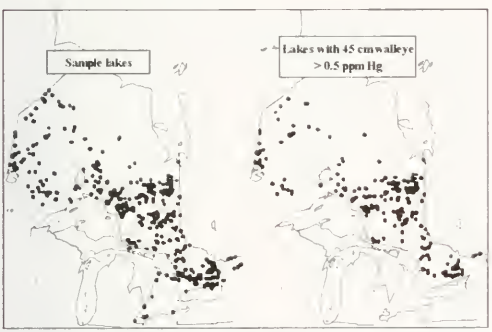


**Figure 2** Distribution of walleye lakes affected by mercury.

## WHERE DOES MERCURY IN LAKES COME FROM?

Until the past few years it was generally assumed that mercury in remote lakes was due to geologic sources. The reasoning was simple. Firstly, the distribution of lakes contaminated with mercury indicated that anthropogenic point sources were not responsible. Secondly, the mercury content of preindustrial sediments demonstrated that mercury has always been present in lakes. The Canadian Geological Survey has shown that mercury in preindustrial sediments is virtually universal. Thirdly, although the mercury content of soils and bedrock is low, there is more than enough to account for the amount observed in lakes. Even very slow release could yield the observed amount in lakes.

Although the logic in the above argument seems straight forward, it fails to consider alternate possibilities and to quantitatively test inferences. For example, wide dispersal of a substance can result from long range transport through the atmosphere. The acid rain issue and catastrophes such as the Chernobyl explosion and fire forever laid to rest doubts about the existence of long range transport of pollutants. Furthermore, the presumption of release from watersheds through mineralization and weathering is hardly justified without evidence. It is well known that watersheds are sinks for trace metals such as lead, copper and cadmium. Much more is deposited on them from the atmosphere than is released to streams.

Given these uncertainties, we set out in the late 1980s, to test the possibility that mercury in lakes was predominantly the result of atmospheric deposition rather than weathering. We used a mass balance approach: we determined the total amount entering lakes through direct precipitation and by runoff, and compared the two fluxes. The results were remarkably straight forward.

In headwater lakes about half of the mercury entering lakes was from direct precipitation and about half from runoff. More importantly, watersheds behaved towards mercury just as they do towards other trace metals: they adsorb most of the mercury deposited on them from precipitation. In other words they are sinks, not sources of mercury. One manifestation of this phenomenon is the relative concentration of mercury in streams and precipitation. The concentration in precipitation averages 5 to 10 times higher than in streams. Without retention of mercury in the watersheds one would expect the average concentration in streams to be about 2 fold higher because of evaporative concentration.

One interesting additional finding of the study was a high correlation between the colour of water and mercury in stream water (Figure 3). Colour is mainly the result of humic material in water. This phenomenon is almost certainly due to the high affinity of humic substances for mercury. As organic matter breaks down and releases soluble organic molecules, some of the adsorbed mercury is released with it.

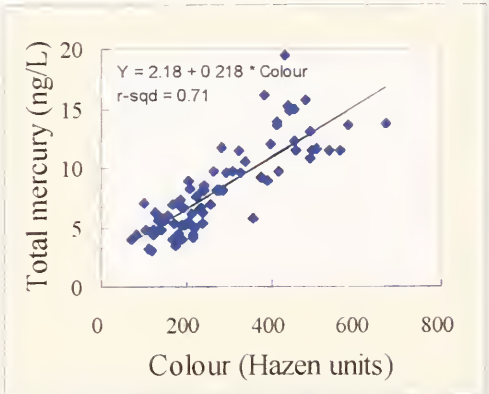


**Figure 3** Correlation of mercury to colour in a small stream over a two year period.

In upland, well drained soil most of the humic matter (and mercury) is adsorbed to soil particles as water percolates through the soil. In wetlands, water has less opportunity to contact mineral layers, and consequently wetlands release much more.

Given that wetlands are a major source of humic material and that mercury is correlated to colour one would expect a relationship between mercury and wetlands. Using a simple, two compartment model of watershed retention, one can show that the relationship between the fraction of mercury exported from the watershed and the fraction of the watershed covered by wetland should be linear. Our data appear quite consistent with this model (Figure 4). This result may explain some of the variation in mercury concentration, in particular some of the "hot spots" such as the Huntsville lakes. These lakes have very large wetlands in their watersheds and high levels of mercury in their fish. It also raises the question about possible other hot spots. There are almost certainly other lakes in Ontario with comparable watersheds. Their concentrations of mercury may be just as high.

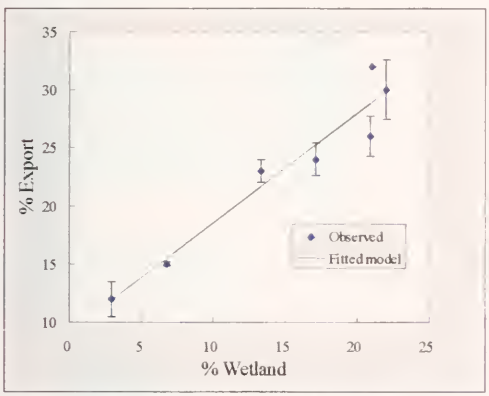


**Figure 4** Relationship of export of mercury to wetlands.

Although most of the mercury deposited on watersheds is retained, it is difficult to determine exactly where the released mercury comes from. It could be from the atmosphere or from bedrock weathering. The association of mercury in streams with DOC and wetlands is circumstantial evidence that the mercury is derived from atmospheric deposition. If weathering were the main source one would expect upland areas to release more mercury than lowland areas. The opposite is observed.

Even though we cannot directly allocate mercury in streams to particular sources, we can estimate the maximum amount from weathering. A number of studies have estimated the release rates of silicon, calcium and other major elements from weathering in watersheds, and from the ratio of these elements to mercury in bedrock and soil minerals one can make very straightforward calculations of the potential release of mercury. For the types of minerals on the Precambrian Shield the calculations indicate that at most 3 to 12 percent of the mercury from watersheds is derived from weathering.

In addition to mercury in minerals there is a substantial amount of mercury bound to organic matter in soil, but rough calculations suggests that it turns over very slowly. From the density of the soil and its mercury concentration a pool of about 750 $\mu g/m^2$ can be estimated for the A horizon, the organic surface layer of forest soils. There is an additional, smaller pool in the B horizon so collectively the pool of organically bound mercury is probably on the order of 1000 $mg/m^2$. Preindustrial deposition of mercury was probably on the order of 4 to 5 $\mu g/m^2$-y, which leads to an estimated turnover rate of 200 to 250 years. This can be compared to the mean residence time of soil humus in podzols of approximately 250 years. Although the similarity of the numbers may be fortuitous, it is at least consistent with the notion that mercury release from watershed is intimately linked to organic matter decomposition and dissolution.

## HAVE HUMAN ACTIVITIES CONTRIBUTED TO MERCURY IN LAKES?

The answer to this question is yes, although there is still some question about the relative proportions of anthropogenic and natural mercury in the atmosphere. Most investigators indicate at least half of the current emissions in the northern hemisphere are anthropogenic, although it may be as high as 75%. A recent inventory in Ontario put total atmospheric emissions at less than natural emissions, but there is considerable uncertainty in the estimate, largely because the natural emissions are so poorly known. Nonetheless, present data indicate that anthropogenic emissions are not inconsequential, and possible means of reducing of anthropogenic sources merit close attention.

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